JOURNAL OF GEOPHYSICAL RESEARCH, VOL. 105, NO. D4, PAGES 4399–4407, FEBRUARY 27, 2000

Temporal variations of surface regional background ozone over Crete Island in the southeast Mediterranean

G. Kouvarakis, K. Tsigaridis, M. Kanakidou, and N. Mihalopoulos

Environmental and Chemical Processes Laboratory, Department of Chemistry, University of Crete, Heraklion, Greece

Abstract. The first year-round observations of seasonal and diurnal variations of background ozone at a coastal site on Crete Island in the southeast Mediterranean area are presented here. They point out (1) the existence of a well-defined seasonal cycle with maximum during summer months, (2) the presence of elevated O_3 levels (up to 80 ppbv) during daytime and over time periods of several days, and (3) the dependence of O_3 mixing ratios on air mass origin. Comparison with three-dimensional chemistry transport model results shows that during summer the measured O_3 values exceed the calculated by 10-20 ppbv. Inclusion of biomass burning and biogenic volatile organic emissions in the model could partly offset the discrepancy between model results and observations.

1. Introduction

Ozone (O_3) is known to be an important greenhouse gas [*Intergovernmental Panel on Climate Change*, 1995; *Chalita et al.*, 1996; *Roelofs et al.*, 1997] and a pollutant [*Seinfeld and Pandis*, 1997]. The effects of O_3 on humans are relatively well established (respiratory problems, irritation of eyes, headaches, etc.) and they have led to the adoption of legislation, which sets upper limits on human exposure to O_3 levels (53 ppbv during 8 hours for the European Union (EU) countries). In the troposphere, O_3 is transported from the stratosphere and it is also photochemically formed by reactions of its precursors (nitrogen oxides; NO_x; carbon monoxide; CO; volatile organic compounds; VOCs, including methane; CH_4). The photochemical production of O_3 in the troposphere occurs by photolysis of nitrogen dioxide NO_2 to atomic oxygen O^3P, which then reacts with molecular oxygen to form O_3. Most of the NO_x is emitted in the atmosphere (mainly by anthropogenic sources) as nitrogen monoxide (NO) which is then converted to NO_2 by reaction with O_3 and peroxy radicals (RO_2) formed during CO and volatile organic compound (VOC) oxidation. Emissions of O_3 precursors by human activity have modified the budget of tropospheric ozone over the past 130 years [*Volz and Kley*, 1988] leading to a net increase in background O_3 (see compilation by *Logan* [1994] for the past 20 years). In the boundary layer, deposition processes are an important sink for O_3 which has therefore a short lifetime due to this procedure of the order of a few days. On the contrary, in the free troposphere the lifetime of tropospheric O_3 governed by photochemistry is relatively long with an annual mean value of about 40 days and strongly depends on the season. It is about a factor of 10 shorter in the summer than in the winter when it can be as long as about 200 days in the midlatitudes [*Liu et al.*, 1987]. Thus midlatitude O_3 can be transported zonally and also toward lower latitudes and affect distant areas. Transport of O_3 is more efficient during winter when simultaneously NO_x natural emissions are substantially small and thus O_3 chemical production is mainly due to anthropogenic precursors. This O_3 accumulates during winter and could partly explain the observed spring maximum that is usually attributed to stratospheric intrusion [*Liu et al.*, 1987].

Crete island located at the southeast edge of Europe is receiving during most of the year air masses influenced by human activity from central and eastern Europe [*Mihalopoulos et al.*, 1997]. According to global model calculations, the eastern Mediterranean where Crete is located is also an area where important climatic changes are occurring due to aerosols [*Charlson et al.*, 1991] and possibly due to O_3 [*Chalita et al.*, 1996; *Roelofs et al.*, 1997]. The special meteorological conditions dominating almost year round over the eastern Mediterranean (intensive sunlight, high temperatures, etc.) can enhance photochemistry in the atmosphere and result in high ozone levels.

Little is known about regional background O_3 mixing ratios over Greece and generally over the eastern Mediterranean area. Until now, there is no systematic study to determine regional background O_3 levels over continental rural and coastal locations in Greece and their seasonal and temporal variability. Only short campaigns for measuring the background ozone in the area have been performed [*Kallos et al.*, 1996; *Suppan et al.*, 1998; *Zerefos et al.*, 1998; *Alper-Siman Tov et al.*, 1997]. The only systematic reported works on regional background O_3 measurements are based on a 6-(April to October) and 7-month data (June to December 1995) collected at Messorougion (Achaia) [*Glavas*, 1999] and Pertouli (Trikala) respectively, both rural areas in the continental Greece [*Kourtidis et al.*, 1997]. These data show the presence of high O_3 levels (50 ppbv and higher) during summer and over relatively long periods of the day.

To experimentally determine the background surface ozone over nonurban areas of southern Greece in the southeast Mediterranean area and to understand the major factors that control its levels, continuous measurements of tropospheric O_3 have been performed at a coastal site of the island of Crete

Paper number 1999JD900984.
0148-0227/00/1999JD900984$09.00

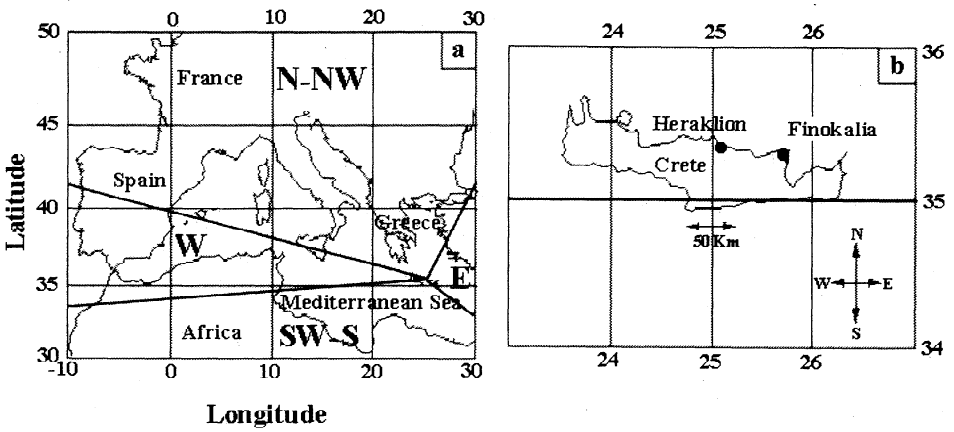

Figure 1. (a) Location of Crete in the Mediterranean Sea and wind sectors used to classify the 5-day back trajectories arriving at Finokalia station. (b) Location of Finokalia and Heraklion on the island of Crete.

since September 1997. The ozone observations are analyzed on the basis of the origin of the sampled air masses and are compared both with measurements in the center of Heraklion City and with the results of three-dimensional (3-D) chemistry/transport models focusing on the eastern Mediterranean area.

2. Experiment

The main sampling station is situated at Finokalia (35° 24' N, 25° 60' E) in the northern coast of Crete (Figure 1). The nearest largest urban center is Heraklion with 150,000 inhabitants at 70 km westward Finokalia. Finokalia station is located at the top of an elevation (130 m) facing the sea within the sector of 270° to 90°. No human activities occur at a distance shorter than 20 km within the above mentioned sector. O_3 measurements have been also performed in the center of Heraklion City by the Prefecture of Heraklion. For the sampling period, meteorological data from the Finokalia station as well from the Heraklion airport are available. In addition, air mass back trajectories are calculated by using a three-dimensional atmospheric transport model [*Ramonet et al.*, 1996] and meteorological data analyzed by the European Centre for Medium-Range Weather Forecasts. Details on these calculations are given by *Ramonet et al.* [1996] and *Mihalopoulos et al.* [1997].

At Finokalia, ozone measurements are made by using a Dasibi 1080 AH analyzer. Since July 1998 a Thermoelectron (Model 49S) is running in parallel. The instruments are mounted inside a small building, directly exposed to the north sector. Air is drawn outside of the building from about 3-4 m above the ground individually for each instrument, using Teflon tubes. The O_3 data are obtained every 10 s. They are averaged and registered every 5 min. In general, the standard error of the mean of the 5-min averages is around 1-2%. Thus all individual 5-min means with a standard error of the mean higher than 20% (i.e., more than a factor of 10 than usual) have been removed from the present analysis, suspected to be the subject of electrical interference. Applying this criterion of data selection, less than 10% of the whole data set has been removed. Comparing all simultaneously collected data and after the previously described data filtering, the agreement between Dasibi and Thermoelectron analyzers for a total of more than 25,000 pairs of 5-min averages is found to be better than 4%.

O_3 measurements have been also performed at Heraklion by the Prefecture of Heraklion using a Dasibi 1008 RS ozone analyzer situated in a van in the center of the city. The two Dasibi units used at Finokalia and Heraklion for this study were compared for several hours and for O_3 mixing ratios ranging between 50 and 80 ppbv; the agreement was found to be better than 6%.

The selection of ozone data under low NO_x conditions at Heraklion requires particular attention since local traffic and human activity influence O_3 mixing ratios. NO_x has been measured at Heraklion by using a Dasibi NO_x analyzer and calibrated on a weekly basis using a dynamic gas calibration system and NO standards. An inverse regression between O_3 and NO_x is observed for the whole period: the highest NO_x levels correspond to the lowest O_3 levels. This situation is mainly due to O_3 consumption by NO, resulting from traffic and other human activities. Thus to retrieve the O_3 monthly mean value under low NO_x conditions for Heraklion, either the intercept of the curve or the mean value of the O_3 corresponding to "low" NO_x mixing ratios has to be used. The second approach has been chosen here because the relationship between O_3 and NO_x is not linear. The monthly mean O_3 value is therefore calculated by averaging all the O_3 values that correspond to NO_x levels lower than 3 ppbv. The above NO_x mixing ratio is roughly twice the mean value observed at Finokalia by a Thermo Environmental 42C NO_x analyzer (N. Mihalopoulos et al., unpublished data, 1999) during the August-November 1998 period. The 3-ppbv level has been retained to characterize relatively low NO_x conditions, since there are not enough cases with NO_x lower than 1.5 ppbv to allow a statistical treatment of O_3 data at Heraklion.

3. Results and Discussion

3.1. Meteorological Description

In Figure 2 the meteorological situation in the eastern Mediterranean area is summarized. Figure 2a presents the seasonal variation of temperature, wind speed, and rain height

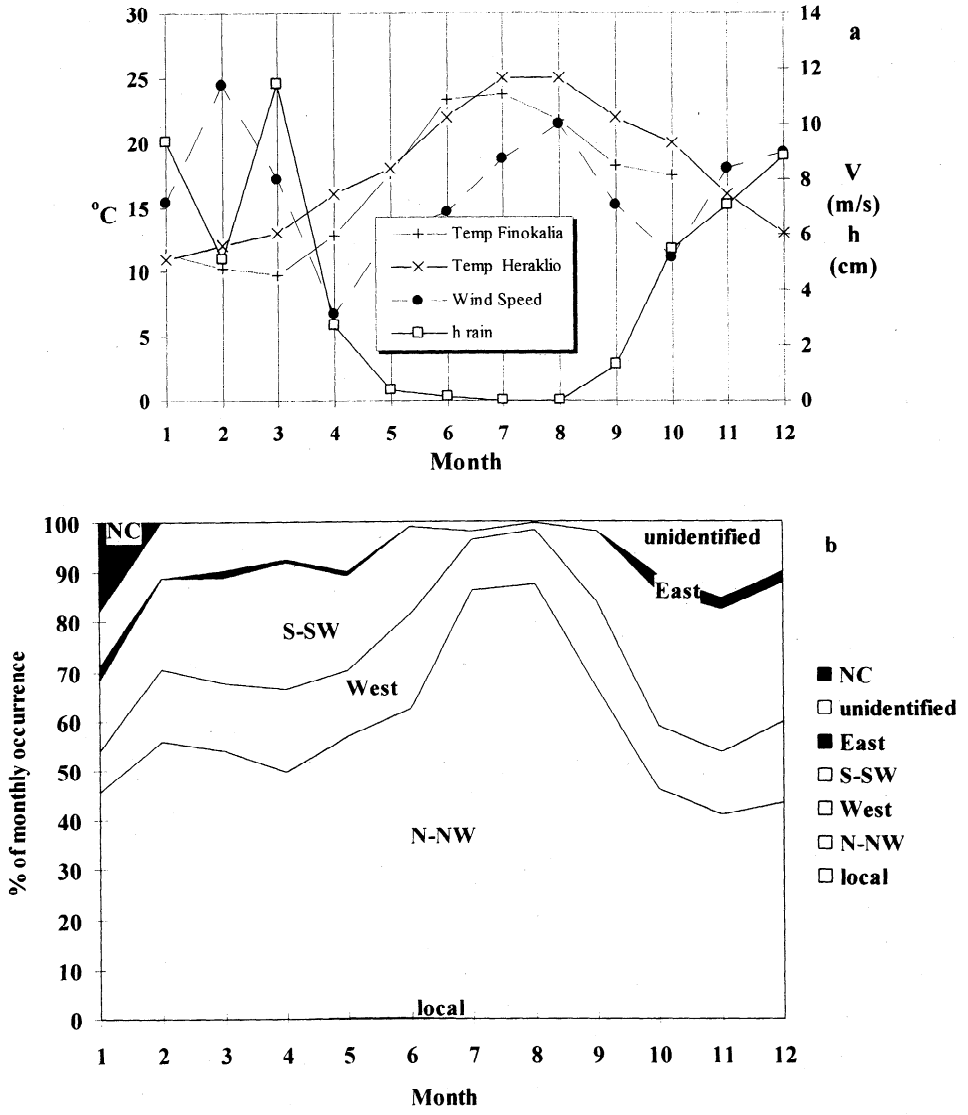

Figure 2. (a) Monthly mean observed temperature at Finokalia in °C (pluses); monthly mean observed temperature at Heraklion airport in °C (crosses); wind speed at Finokalia in m s^{-1} (solid circles); height of rain at Finokalia in centimeters (open squares). (b) Classification of the 5-day back trajectories arriving at Finokalia over an 8-year period from 1990 to 1997, according to the wind sectors shown in Figure 1a (NC; non-classified; local; air masses originating from less than 100 km around Finokalia).

at Finokalia during the 1997-1998 period, except the temperature for the time period from November to December 1998, due to technical problems. For temperature, statistic data from the Heraklion airport for the last 25 years are also presented. Figure 2b shows the seasonal variation of the wind origin based on a classification of 5-day backward trajectories for the 8-year period (1990-1997) performed as described by *Mihalopoulos et al.* [1997] for the sectors shown in Figure 1. From Figure 2a the existence of two well-distinguished seasons equally distributed within the year is obvious: The dry season (from May to September) and the wet season (from October to April). From the air mass origin point of view (Figure 2b) the dry season is mainly characterized by winds of north/northwest direction (central and eastern Europe and Balkans) which from July to September correspond to 90% of the wind occurrences over this period. Note that the east sector is of negligible importance all year round. During the warm months the wind speed presents a second maximum, as high as that observed during winter (Figure 2a) Thus the absence of precipitation and the increased wind speed during the dry season could favor transport and photochemical transformation of ozone precursors from long distances, as it has been observed for aerosols [*Mihalopoulos et al.*, 1997]. The dry season is also characterized by high temperatures and intensive sunlight, favoring photochemistry. During the wet season the prevalence of N/NW sector is less pronounced, and especially in March/April and in October/November winds from the north/northwest, south/southwest (Africa), and west sectors (marine influence) are roughly equally distributed.

3.2. Seasonal Variation of Ozone

Figure 3 presents the seasonal variations of the O_3 observed at Finokalia and selected "low NO_x" Heraklion data

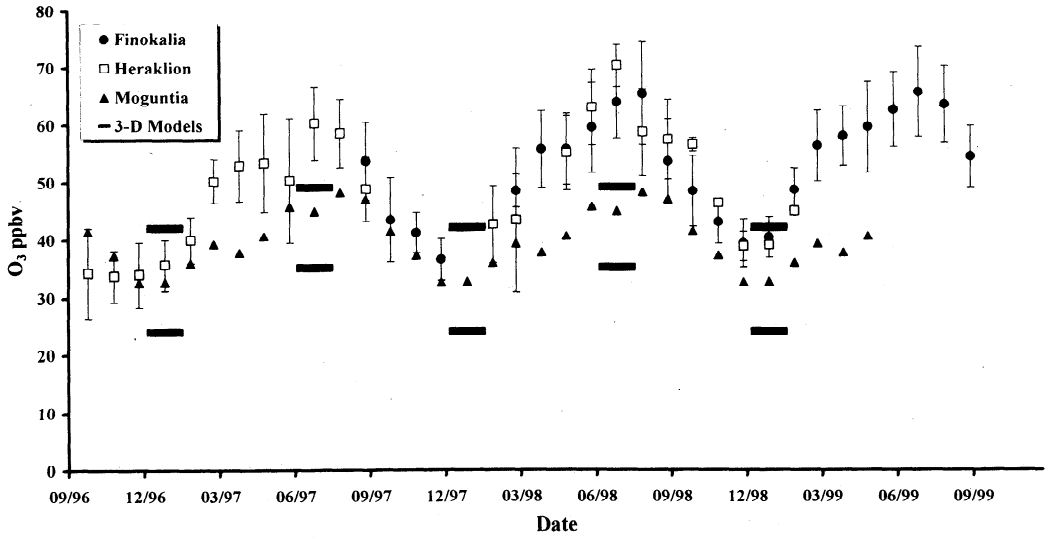

Figure 3. Monthly mean observations of O_3 at Finokalia since October 1997 (solid circles) and in Heraklion City since October 1996 (open squares correspond to monthly mean values of the data selected as discussed in section 2.3 and bars to their standard deviation). Solid triangles correspond to the 3-D MOGUNTIA model calculations, and horizontal bars indicate the range of the global 3-D models given by *Kanakidou et al.* [1999a, b].

since September 1997 and September 1996, respectively. A well-distinguished seasonal cycle is deduced both from Heraklion and Finokalia data, with minimum values around 35 ppbv during winter and maximum up to 70 ppbv during summer. A reasonable good agreement exists between Finokalia and Heraklion data (Figure 3). More precisely, during the dry period (May to September) the mean O_3 values at Finokalia and Heraklion were 59±5 ppbv and 61±6 ppbv, respectively. This agreement indicates that the observed signal at Finokalia is not a local phenomenon.

The observed seasonal trend in O_3 at Finokalia is in good agreement (in terms of relative magnitude) with that reported for several rural European locations [*Janach*, 1989; *Logan*, 1994; *European Monitoring and Evaluation Programme* (EMEP), 1998]. In absolute terms, both the summer and winter values observed at Finokalia are about 10-15 ppbv higher than those observed at Pertouli (39°33'N, 21°28'E) a forested site at 1300 m elevation in the central Greece [*Kourtidis et al.*, 1997]. The summer values are also 15-20 ppbv higher than those observed at Messorougion (38°01'N, 22°15'E) a forested site at 1070 m elevation in western Greece [*Glavas*, 1999]. On the other hand, the summer values agree very well with those observed at the island of Agios Eustratios in the northern part of the Aegean Sea during the PAUR campaign performed from July 1 to 15, 1997 [*Zerefos et al.*, 1998]. According to the dispersion calculations by *Kallos et al.* [1998], during summer both Crete and Agios Eustratios are located in the north-south flow of air masses which is the prevailing pattern for the whole eastern Mediterranean basin except the Levantine Sea (region around Cyprus). Thus the observed high summertime O_3 levels over Crete should be characteristic for the major part of the eastern Mediterranean area. Unfortunately, lack of published long-term measurements in the area prohibit systematic comparison of our data. Based on a recent compilation of O_3 data [*EMEP*, 1998], the O_3 levels observed at Finokalia during the dry period are among the highest reported for rural areas in Europe.

3.3. Comparison With 3-D Model Results

It is interesting to investigate the capability of chemistry/transport models to simulate such high background O_3 levels as these observed at Finokalia. For this purpose, the range of thirteen 3-D chemistry/transport global model estimates for the eastern Mediterranean region has been also depicted in Figure 3 for January and July. These models that participated at the Global Integration Modeling/International Global Atmospheric Chemistry (GIM/IGAC) intercomparison exercise, have significant differences in the representation of transport and chemistry processes as discussed by *Kanakidou et al.* [1999a, b] and references therein.

As shown in Figure 3, the range of these models captures the 30-40 ppbv levels of O_3 during wintertime, that is, under relatively low photochemical activity, although some of them underestimate wintertime O_3 by about 40%. On the other hand, most of them (with only two exceptions not shown in Figure 3) are not able to simulate the elevated summertime O_3 levels of the order of 60-70 ppbv since the maximum model estimates reach only the 50 ppbv level. In addition, most models, when their horizontal resolution allows distinction, simulate higher O_3 values in Greece over continents than over sea, in contradiction with the observations discussed in the previous section. Finally, no systematic N/S gradient in O_3 can be derived from the model calculations. These deficiencies of the models can not be attributed to a unique factor since models with relatively high resolution, good representation of meteorology, and rather simple chemistry are not always performing better than those with lower resolution or medium representation of meteorology and rather detailed chemistry. Note that a reference high-resolution model with good meteorology and detailed chemistry is not yet available. Thus the clear statement from this comparison is that ozone source in the southeast Mediterranean by long-range transport and/or local photochemistry might be underestimated in most global models. Such deficiency may be linked to the emission of O_3

precursors adopted in the models, in particular these of biogenic volatile organics and NO_x and VOC emissions from biofuel and shipping, which are poorly documented for the eastern Mediterranean [*Kanakidou et al.*, 1999a; *Kourtidis et al.*, 1999; *Lawrence and Crutzen*, 1999]. Uncertainties in emissions by biofuel will contribute to model deviations from observations, year round. On the other hand, biogenic organic emissions are expected to contribute mainly during summer when high temperatures and solar intensity enhance these natural emissions. In addition, volatile organic compound oxidation, in particular that of biogenics, is not well understood. Thus VOC representation in global models based on a limited number of compounds is a source of major uncertainties and errors.

3.4. Impact of Ozone Precursor Emissions

To further analyze the differences between observations and model results, one among these models, the global 3-D chemistry/transport model MOGUNTIA has been used [*Zimmermann*, 1988; *Crutzen and Zimmermann*, 1991; *Kanakidou and Crutzen*, 1999; *Poisson et al.*, 1999]. MOGUNTIA is a climatological Eulerian model with a resolution of 10° latitude by 10° longitude and 10 vertical layers of 100 hPa thickness, located between the Earth surface and 100 hPa. The chemical scheme of the MOGUNTIA model considers the background $O_3/NO_x/OH/CO/CH_4$ chemistry and the oxidation of C_2-C_3 alkanes, light alkenes, isoprene (C_5H_8) used to represent the group of biogenic hydrocarbons, and *n*-butane (C_4H_{10}) used to represent other nonmethane hydrocarbons (NMHC), as described by *Poisson et al.* [1999] and *Kanakidou and Crutzen* [1999]. The chemical scheme is rather detailed for a global 3-D model taking into account about 150 photochemical reactions involving 75 compounds.

Note that in this model as in many other global models, extratropical biomass burning is not explicitly taken into account. The main anthropogenic source of NO_x considered in these models for the extratropical areas is therefore linked to technological emissions. However, biomass burning occurring during summer months over the whole Mediterranean area is expected to be a strong source of ozone precursors and aerosols in this area.

To evaluate the importance of hydrocarbon chemistry and of NO_x anthropogenic emissions in O_3 formation over the studied area, the O_3 levels at Finokalia have been calculated by the model for four different simulations: (1) taking into account CO, CH_4, and nonmethane hydrocarbon chemistry (basic), (2) taking into account only CO and CH_4 chemistry ($CO+CH_4$), (3) as the "basic" case but with double global industrial emissions of NO_x (NO_xind*2), and (4) as "basic" case but neglecting global emissions of NO_x from technological sources (NO_xind*0). An additional simulation (5) has been performed by neglecting photochemistry in the troposphere and considering transport from the stratosphere to the troposphere as the only source for tropospheric O_3 and dry deposition as its only sink. The results of the first four simulations are depicted in Figure 4.

The MOGUNTIA model ("basic" simulation) successfully simulates the fall and early winter O_3 observations at Finokalia (Figure 4), although the model significantly underestimates the spring and summertime high mixing ratios of O_3 observed in the area. Thus the model when critically used can be a useful tool for analysis of the O_3 observations and identification of the factors that control O_3 levels in the eastern Mediterranean.

Comparison between the simulations (1), (3), and (4) which differ in the amount of NO_x emissions by technological sources demonstrates the importance of NO_x in ozone levels. According to these results, the technological emissions of NO_x are responsible of a buildup of about 20 ppbv O_3 in summer, calculated as the reduction in O_3 when neglecting these emissions. However, doubling industrial NO_x does not lead to more than 5 ppbv of increase in O_3. This reflects the nonlinearity of the NO_x/O_3 chemical system in a NO_x-limited environment.

Another factor with significant impact on O_3 levels is the

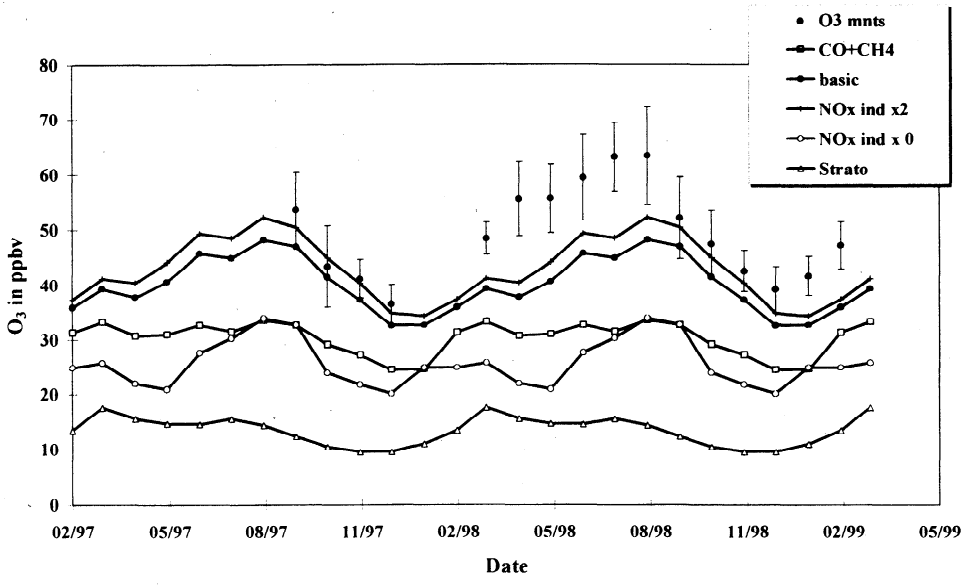

Figure 4. Comparison of the monthly mean observations of O_3 at Finokalia (solid circles, bars show the standard deviation) with the 3-D MOGUNTIA model results. Solid circles with solid line correspond to the "basic" simulation; pluses with solid line correspond to double industrial NO_x simulation; open circles with solid line correspond to no industrial NO_x simulation and open square with solid line correspond to $CO+CH_4$ simulation. Units are ppbv.

Table 1. O_3 Mixing Ratios at Finokalia, Averaged Within a Sector and the Corresponding Standard Deviation.

	North/Northwest		West		South/Southwest	
Date	Ozone	s.d.	Ozone	s.d.	Ozone	s.d.
August 1997	58.1	1.7	40.4	2.9	-	-
September 1997	54.6	6.2	-	-	-	-
October 1997	47.1	8.5	39.1	3.7	33.2	2.9
November 1997	45.0	2.9	40.6	2.2	-	-

Units in ppbv. Dash means no air mass origin from this sector during that time period. Abbreviation s.d., standard deviation.

presence of nonmethane hydrocarbons (NMHC). Their importance is shown by comparison between the "basic" and the "CO+CH_4" simulations. As shown in Figure 4, about one third of the observed O_3 mixing ratios during summer is related to NMHC oxidation. NMHC contribution is reduced to one fifth of the total O_3 during winter. Further increase in NMHC biogenic emissions by 50% (not shown in Figure 4 for clarity) does not significantly affect O_3 levels, indicating thus that, as previously mentioned, the studied environment is limited by NO_x and not by hydrocarbon abundance. Finally, the importance of tropospheric photochemistry on O_3 levels is evaluated by comparison between the "basic" simulation and simulation (5) performed neglecting all photochemical reactions in the troposphere. When photochemistry is neglected in the troposphere, annual mean O_3 mixing ratios of 13±3 ppbv are calculated for Finokalia. However, the horizontal resolution of the model is too coarse to solve synoptic disturbances in the upper troposphere related to stratosphere/troposphere exchange events, and therefore the parameterization of the stratospheric ozone influx is quite poor. Thus the results of simulation (5) have to taken with caution. Moreover, the value of 13±3 ppbv represents an upper limit because ozone photochemical destruction is neglected for this simulation. Since this value is 3 times lower than the 40±5 ppbv of O_3 for the "basic" simulation, it shows the importance of photochemical buildup of O_3.

3.5. Impact of Air Mass Origin

To investigate the potential locations of the sources of ozone precursors that affect the station of Finokalia, a thorough analysis of observations is performed for selected time periods based on back trajectory calculations. As discussed in paragraph 3.1, during March/April and October/November, winds from all the main sectors, that is, north/northwest (Europe and Balkans), south/southwest (Africa), and west (marine influence) are roughly equally distributed. Taking into account the relatively low frequency of precipitation events during these months (Figure 2b), as well as the high insolation which favors the photochemical production of O_3, April and October consist of ideal periods to study the role of air masses origin on O_3 levels. Figure 5 presents the observed O_3 variation from October 1 to 16, 1997, a period with no rain event, since the first precipitation event of October 1997 took place on October 17. Selected 5-day back air mass trajectories, calculated for 0000 or for 1200 UT (UT = local time - 2 hours), are also presented in Figure 5. An important variability in O_3 mixing ratios, from 27 up to 64 ppbv (more than a factor of 2), is clearly shown. All changes in the air mass origin are associated with important changes in O_3 mixing ratios. The lowest O_3 values are systematically associated with the south/southwest sector and the highest with the north/northwest sector.

Table 1 summarizes the monthly mean and the standard

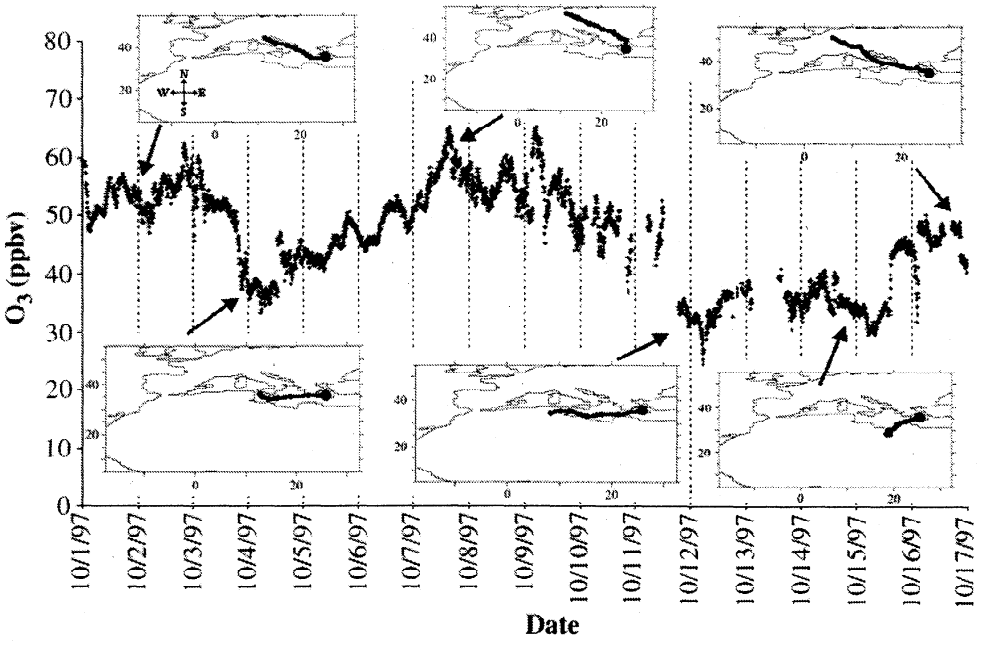

Figure 5. Variation of observed O_3 mixing ratios (ppbv) at Finokalia from October 1 to 17, 1997, and selected 5-day back trajectories of air masses arriving at Finokalia during this period.

deviation of the observed O_3 mixing ratios as a function of the wind sector from August to November 1997. The lowest O_3 levels are indeed associated with the south/southwest sector and the highest with the north/northwest sector. The low O_3 levels observed during the south/southwest sector are in agreement with the background O_3 mixing ratios calculated by global 3-D chemistry/transport models for the area (see Figure 4).

The west sector (marine influence) results in O_3 mixing ratios slightly higher than the south/southwest sector. This dependence of atmospheric compound levels on air mass origin has been also observed in our preliminary study of the ionic composition of aerosols conducted at Finokalia over a year (1995-1996) [*Mihalopoulos et al.*, 1997]. Indeed, non-sea-salt sulfate (nss-$SO_4^=$) mixing ratios associated with the north/northwest sectors were always higher by a factor of 2 to 3 than nss-$SO_4^=$ mixing ratios measured when south/southwest air masses occurred. Thus the high O_3 mixing ratios associated with north/northwest winds result from buildup of photooxidants during transport from mainland Greece, Balkans, and central Europe.

3.6. Diurnal Variation of Ozone

A first attempt to investigate the possible existence of diurnal variation of O_3 at Finokalia was performed for fall 1997, for which a detailed air mass origin analysis was available. Indeed, since air mass origin has an important impact on O_3 levels, any bias that might be induced by the factor "sector" has to be removed before investigating a possible diurnal signal. Figure 6 presents the diurnal mean variation of observed O_3 for October 1997 for the three main sectors. Each bin is the average of hourly mean O_3 for 6, 3 and 4 independent 24-hour events with north/northwest, west and south/southwest winds, respectively. For clarity, the normalized measured O_3, that is, O_3 mixing ratio divided by the corresponding diurnal mean O_3 mixing ratio, is depicted in Figure 6. The absolute diurnal mean values are given in Table 1. A weak, nonsignificant diurnal variation exists for all sectors with slightly lower values in the morning hours (between 5 and 11 hours, local time) and higher in the afternoon (between 13 and 19 hours). The diurnal amplitude defined as the difference between the normalized minimum and maximum values observed within each sector does not exceed 10%, which corresponds to 4-7 ppbv, depending on the sector. This amplitude is slightly higher than the mean of the standard deviation (s.d.) of the observations under northern wind conditions (6%) but is similar to the mean s.d. of the observations under western (8%) and southern wind (10%) regimes. These results indicate only a weak local photochemical buildup of ozone in fall, which is more important under northern wind conditions probably due to the higher NO_x and NMHC levels. The high wind speed could also prohibit a local photochemical buildup of O_3. Moreover, the relatively high nighttime values of O_3 are due to its low deposition velocity above the sea compared to continents.

The absence of significant diurnal signal under the southern wind conditions, despite the fact that the air masses travel across the island for few tens of kilometers before reaching our sampling station, is due both to the strong wind speeds (up to 45 m/s) associated with this wind conditions and to the absence of important cities or important anthropogenic activities in the southern part of the island. The insignificant diurnal variation of O_3 observed under northern wind conditions clearly indicates the dominant role of long-range transport of pollutants in ozone budget over the studied area.

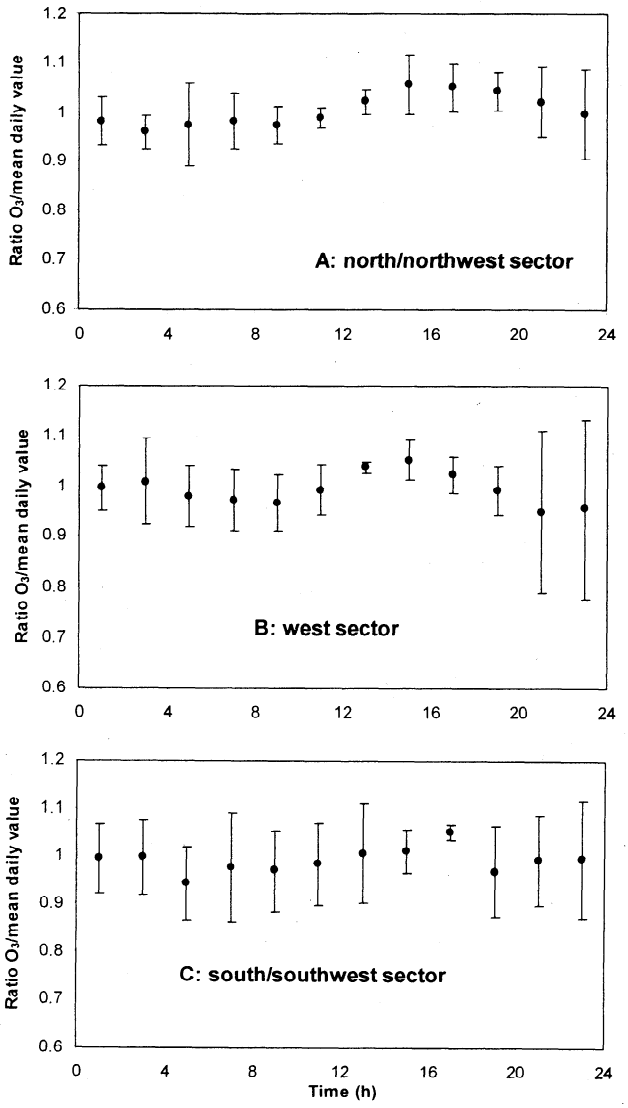

Figure 6. Diurnal variation of O_3 mixing ratios at Finokalia normalized to the corresponding diurnal mean value for the three main wind sectors: (a) north sector, (b) west sector, and (c) south/southwest sector.

Finally, the absence of recirculation of air masses above the island as indicated by the meteorological data can also account for the absence of significant diurnal variation. Indeed, the situation of seashore elevated ozone due to wind recirculation has been previously reported by various authors and for various locations in the Mediterranean area. For instance, *Millan et al.* [1991] and *Alper-Siman Tov et al.* [1997] have documented this situation for selected areas both in the western (Spanish coast) and the eastern Mediterranean area (Israeli coast) during summer. They noted that recirculation of air masses with low wind speeds related to sea and land breeze phenomena can result in very high O_3 levels. However, such situations are accompanied by a net diurnal change in the wind direction, which was not observed at Finokalia. In addition, the high wind speeds observed during summer in the area (Figure 2a) prohibit the establishment of sea/land breeze phenomena. Thus the elevated O_3 levels observed at Finokalia during summer could

not be related to recirculation of air masses. The ongoing measurements of O_3 precursors at Finokalia in conjunction with air mass origin analysis will contribute to improve the understanding of O_3 diurnal variations at this site.

3.7. Comparison Between O_3 Levels and Products of NO_x Oxidation

When ozone mixing ratios are plotted as a function of the NO_x oxidation products, the scatter of data due to differences in the photochemical aging of the sampled air masses, whether due to sampling of fresh emissions or to seasonal effects, should minimize [*Trainer et al.*, 1993]. The reason is that both O_3 and NO_x oxidation products are similarly affected by the previously mentioned factors. At Finokalia, particulate NO_3^- has been continuously measured since October 1996 and HNO_3 from October 1996 to May 1997. Samples for particulate NO_3^- and gaseous HNO_3 analysis were collected over 2-day periods using Teflon filters and annular denuders coated with Na_2CO_3, respectively. Details on the analytical setup are given by *Lawrence and Koutrakis* [1994]. Both compounds present a distinguished seasonal variation with minimum during winter (mean value around 0.2 ppbv) and maximum during summer (mean value around 1 ppbv) for both HNO_3 and NO_3^-. This seasonal cycle is on line with that observed for ozone. Peroxyacetylnitrate (PAN), another important oxidation product of NO_x, was not measured at Finokalia. An attempt to estimate PAN mixing ratios was made on the basis of the O_3 measurements at Finokalia and by using the empirical equation given by *Kourtidis et al.* [1997]. This equation has been deduced from more than 700 measurements performed on an island downwind Athens and roughly 300 km north-northwest of our sampling site. This is the closest to the Finokalia site for which PAN measurements have been reported in literature. However, this ratio has to be used with caution since it depends on meteorological conditions and NO_x levels [*Kourtidis et al.*, 1993]. Figure 7 presents the monthly mean ozone mixing ratios as a function of the monthly mean mixing ratios of NO_x oxidation products and particularly of (1) HNO_3, (2) the sum of HNO_3 and NO_3^-, and (3) the sum of HNO_3, particulate NO_3^-, and calculated PAN. All three regression coefficients are significant, since they exceed values of 0.86 (r^2, for 9-10 number of points). Moreover, the origin of the three regression lines, which corresponds to the background mixing ratios of O_3 of about 34 ppbv, varies very little from 32.7 to 34.9 ppbv. This calculated value of about 34 ppbv is in excellent agreement with the mean O_3 value observed during October (close to the Northern Hemisphere solstice) under southern wind influence (33.2 ppbv). It agrees also very well with the background O_3 mixing ratio in the northern latitudes which is around 35 ppbv (see, for example, the Mace Head station [*EMEP*, 1998; *Derwent et al.*, 1998]). Finally, the slope of the regression of O_3 versus the sum of mixing ratios of HNO_3, particulate NO_3^- and PAN is 14.2. According to *Trainer et al.* [1993], this ratio corresponds to the number of O_3 molecules produced per NO_x molecule oxidized, also called ozone production efficiency. As shown in Figure 7, consideration of PAN mixing ratios (and any possible error introduced by calculating its mixing ratios for Finokalia, as mentioned below) do not affect this ozone production efficiency by more than 20%. The value of 14.2 compares well with those calculated for several rural areas as well in the United States (12.3 [*Olszyna et al.*, 1994]; 12.0 [*Hastie et al.*, 1996]) and Caesarea (Israel coast, also in the eastern Mediterranean; 10.9 [*Alper-Siman Tov et al.*, 1997]).

4. Conclusion

The first observations of the seasonal variation of background ozone at a coastal site on Crete Island in the southeast Mediterranean area have been presented here. They point out (1) the existence of a well-defined seasonal cycle with maximum during summer months, (2) the presence of elevated O_3 levels (up to 80 ppbv) during summertime and over time periods of several days, (3) the absence of any important diurnal cycle indicating that local photochemistry has a rather weak impact on O_3 levels, and (4) the dependence of O_3 mixing ratios on air mass origin. The correlation between ozone and NO_x oxidation products shows that about 14 molecules of ozone are produced per molecule of NO_x oxidized in the studied air masses. This reflects the high ozone production efficiency of NO_x in the air masses arriving at Finokalia. A comparison with 3-D chemistry transport model results shows a reasonable agreement between simulations and observations during fall and winter. During

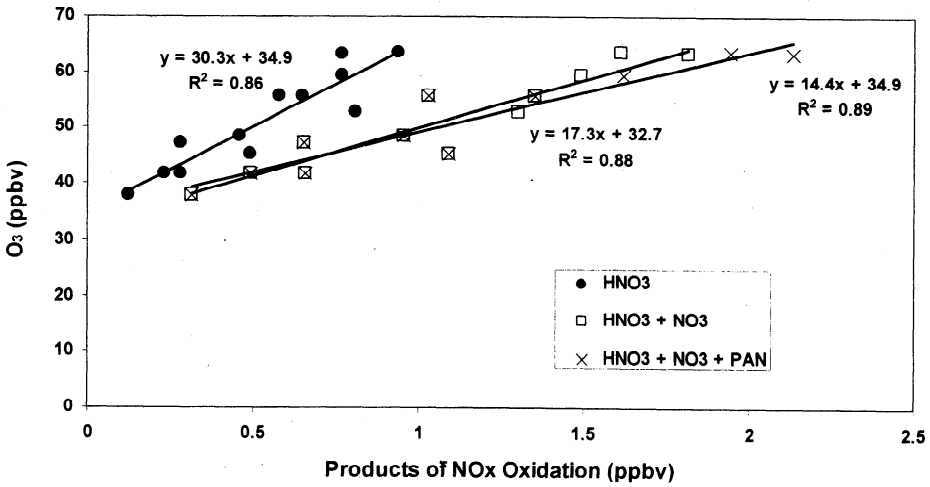

Figure 7. Observed O_3 levels as a function of the mixing ratios of products of NO_x oxidation at Finokalia. Solid circles, O_3 versus HNO_3; open squares, O_3 versus HNO_3+NO_3; crosses, O_3 versus HNO_3+NO_3+ PAN. Units are ppbv.

spring and summer the measured O_3 mixing ratios exceed the calculated values. Important biomass burning in the area in conjunction with biogenic volatile organic emissions could account for these significant differences during summer. These results point out the need for (1) more accurate parameterization of VOCs chemistry in the models and (2) systematic experimental studies of the location and the intensity of the VOC and NO_x sources in the eastern Mediterranean.

Acknowledgments. We thank Hans-Peter Dorn and Bernard Bonsang for collaboration and valuable help in measuring O_3 at Finokalia station. M. Tsorbatzakis and M. Voutirakis from the Prefecture of Heraklion for providing the O_3 and NO_x data of Heraklion City, the Municipality of Neapolis, and especially the mayor, N. Kastrinakis for facilities at Finokalia, and the University of Crete (ELKE) for financial support. M.K. expresses gratitude to the LSCE (CNRS-CEA) and IDRIS for computing facilities.

References

Alper-Siman Tov, D., M. Peleg, V. Matveev, Y. Mahrer, I. Seter, and M. Luria, Recirculation of polluted air masses over the East Mediterranean coast, *Atmos. Environ., 31*, 1441-1448, 1997.

Chalita, S., D.A. Hauglustaine, H. Le Treut, and J.-F. Muller, Radiative forcing due to increased tropospheric ozone concentrations, *Atmos. Environ., 30*, 1641-1646, 1996.

Charlson, R.J., J. Langner, H. Rodhe, C.B. Leovy, and S.G. Warren, Perturbation of the Northern Hemisphere radiative balance by backscattering from anthropogenic sulfate aerosols, *Tellus, 43AB*, 152-163, 1991.

Crutzen, P.J., and P.H. Zimmermann, The changing photochemistry of the troposphere, *Tellus, 43AB*, 136-151, 1991.

Derwent, R.G., P.G. Simmonds, S. Seuring, and C. Dimmer, Observation and interpretation of the seasonal cycles in the surface concentrations of ozone and carbon monoxide at Mace Head, Ireland from 1990 to 1994, *Atmos. Environ., 32*, 145-157, 1998.

European Monitoring and Evaluation Programme (EMEP), Transboundary photooxidant air pollution in Europe: Calculations of tropospheric ozone and comparison with observations, *Rep. EMEP/MSC-W*, Norway, July 1998.

Glavas, S., Surface ozone and NO_x concentrations at a high altitude Mediterranean site, Greece, *Atmos. Environ., 33*, 3813-3820, 1999.

Hastie, D.R., P.B. Shepson, N. Reid, P.B. Roussel, and O.T. Melo, Summertime NO_x, NO_y and ozone at a site in rural Ontario, *Atmos. Environ., 30*, 2157-2165, 1996.

Intergovernmental Panel on Climate Change, *Climate Change 1994*, edited by J.T. Houghton, 339 pp., Cambridge Univ. Press, New York, 1995.

Janach, W.E., Surface ozone: Trends details, seasonal variation, and interpretation, *J. Geophys. Res., 94*, 18,289-18,295, 1989.

Kallos, G., et al., Transport and transformation of air pollutants from Europe to the east Mediterranean, in *Environmental Research Program AVICENNE*, final report, EU, Brussels, 1996.

Kallos, G., V. Kotroni, K. Lagouvardos, and A. Papadopoulos, On the long-range transport of air pollutants from Europe to Africa, *Geophys. Res. Lett., 25*, 619-622, 1998.

Kanakidou, M., and P.J. Crutzen, The photochemical source of carbon monoxide: Importance, uncertainties and feedbacks, *Chemosphere, Global Change Science, 1*, 263-282, 1999.

Kanakidou, M., et al., 3-D global simulations of tropospheric CO distributions: Results of the GIM/IGAC intercomparison 1997 exercise, *Chemosphere, Global Change Science, 1*, 91-109, 1999a.

Kanakidou, M., et al., 3-D global simulations of tropospheric chemistry with focus on ozone distributions: Results of the GIM/IGAC intercomparison 1997 exercise, in *Report to the EU, December 1998, Rep. EUR 18842*, 79pp., EU, Brussels, 1999b.

Kourtidis, K., P. Fabian, C. Zerefos, and B. Rappengluck, Peroxyacetyl nitrate (PAN), peroxypropionyl nitrate (PPN), and PAN/ozone ratio measurements at three sites in Germany, *Tellus, 45B*, 442-457, 1993.

Kourtidis, K., I. Ziomas, C. Zerefos, D. Balis, P. Suppan, A. Vasaras, V. Kosmidis, and A. Kentarchos, On the background ozone values in Greece, in *The Oxidizing Capacity of the Troposphere*, B. Larsen, B. Versino, G. Angeletti eds., *EUR 17482*, 387-390pp., EU, Brussels, 1997.

Kourtidis, K., I.C. Ziomas, B. Rappengluck, A. Proyou, and D. Balis, Evaporative traffic HC emissions, traffic CO and speciated hydrocarbon emissions from the city of Athens, *Atmos. Environ., 33*, 3831-3842, 1999.

Lawrence, M.G., and P.J. Crutzen, Influence of NO_x emissions from ships on tropospheric photochemistry and climate, *Nature, 402*, 167–170, 1999.

Lawrence, J.E., and P. Koutrakis, Measurement of atmospheric formic and acetic acids: Methods evaluation and results from field studies, *Environ. Sci. Technol., 28*, 957-964, 1994.

Liu, S.C., M. Trainer, F.C. Fehsenfeld, D.D. Parrish, E.J. Williams, D.W. Fahley, G. Hubler, and P.C. Murphy, Ozone production in the rural troposphere and the implications for regional and global ozone distributions, *J. Geophys. Res., 92*, 4191-4207, 1987.

Logan, J.A., Trends in the vertical distribution of ozone: An analysis of ozonesonde data, *J. Geophys. Res., 99*, 25,553-25,585, 1994.

Mihalopoulos, N., E. Stephanou, M. Kanakidou, S. Pilitsidis, and P. Bousquet, Tropospheric aerosol ionic composition above the eastern Mediterranean area, *Tellus, 49B*, 314-326, 1997.

Millan, M., B. Artinano, L. Alonso, N. Navazo, and M. Castro, The effect of meso-scale flows on regional and long-range atmospheric transport in the western Mediterranean area, *Atmos. Environ., 25*, 949-963, 1991.

Olszyna, K.J., E.M. Bailey, R. Simonaitis, and J.F. Meagher, O_3 and NO_y relationships at a rural site, *J. Geophys. Res., 99*, 557-563, 1994.

Poisson, N., M. Kanakidou, and P.J. Crutzen, Impact of non methane hydrocarbons on tropospheric chemistry and particular the oxidizing power of the global troposphere; 3-Dimensional modeling results, *J. Atmos. Chem.*, in press, 1999.

Ramonet, M., J.C. Le Roulley, P. Bousquet, and P. Monfray, Radon-222 measurements during the TROPOZ II campaign and comparison with a global atmospheric transport model, *J. Atmos. Chem., 11*, 117-131, 1996.

Roelofs, G.J., J. Lelieveld, and R. van Dorland, A three-dimensional chemistry/general circulation model simulation of anthropogenically derived ozone in the troposphere and its radiative climate forcing, *J. Geophys. Res., 102*, 23,389-23,401, 1997.

Seinfeld, J., and S. Pandis, *Atmospheric Chemistry and Physics: From Air Pollution to Climate Changes*, John Wiley, New York, 1997.

Suppan, P., P. Fabian, L. Vyras, and S.E. Gryning, The behavior of ozone and peroxyacetyl nitrate concentrations for different wind regimes during the MEDCAPHOT-TRACE campaign in the greater area of Athens, Greece, *Atmos. Environ., 32*, 2089-2102, 1998.

Trainer, M., et al., Correlation of ozone with NO_y in photochemically aged air, *J. Geophys. Res., 98*, 2917-2925, 1993.

Volz, A., and D. Kley, Evaluation of the Monsouris series of ozone measurements made at the nineteenth century, *Nature, 332*, 240-242, 1988.

Zerefos C., et al., Final report of the PAUR project, EU, Brussels, 1998.

Zimmermann, P., MOGUNTIA: A Handy global tracer model., in *Air Pollution Modeling and Its Application VI*, edited by H. van Dop, 593-608pp., Plenum Press, New York, 1988.

M. Kanakidou, G. Kouvarakis, N. Mihalopoulos (corresponding author), and K. Tsigaridis, Environmental and Chemical Processes Laboratory, Department of Chemistry, University of Crete, P.O. Box 1470, 71409 Heraklion, Greece. (mariak@chemistry.uch.gr; kouvarak@chemistry.uch.gr; mihalo@chemistry.uch.gr; tsigaridis@chemistry.uch.gr)

(Received April 5, 1999; revised September 7, 1999; accepted September 17, 1999.)